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DEVELOPMENT OF POLYSULFIDE TECHNOLOGY
FOR TREATMENT OF CONCENTRATED SPENT CYANIDE LIQUORS

PROJECT NO. 233PL

prepared for the
Ontario Ministry of the Environment
135 St. Clair Avenue West
Toronto, Ontario
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FEBRUARY 1988

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DEVELOPMENT OF POLYSULFIDE TECHNOLOGY
FOR TREATMENT OF CONCENTRATED SPENT CYANIDE LIQUORS

Research Advisory Committee Project No. 233PL

for Waste Management and Policy & Planning Branches
Ontario Ministry of the Environment
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FEBRUARY 1988

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ABSTRACT

Concentrated spent cyanide liquors can be effectively pre-treated by a reaction with polysulfides. The preliminary work on the subject showed promising results. The purpose of this study was to develop the polysulfide treatment for a practical application. The scope of the work covered: (1) tests for comparison of reactivity of calcium polysulfide and sodium polysulfide at cyanide to polysulfide ratios of 1:1, 1:1.5, and 1:2; (2) tests to examine treatment efficiencies on three different spent cyanide liquors (from zinc plating, copper plating, and cadmium plating); (3) preliminary tests on removal of residual polysulfide from the treated liquors; (4) preliminary leaching tests on the precipitate formed in the cyanide-polysulfide reactions; (5) tests on development of a practical method to produce calcium polysulfide on location at a metal finishing shop; (6) preliminary economic analysis of the treatment; (7) two pilot-scale tests on the application of polysulfide technology at a metal finishing shop.

The experimental results confirmed that the polysulfide reaction was effective at a very broad range of cyanide concentration and presence of metal complexes in the treated liquors. The residual cyanide and metal contents in the reaction products were in the range low enough to discharge them to municipal sewers. Over 95% removal of residual polysulfide from treated liquors could be accomplished by the addition of ferrous sulfate. Metal ion concentrations in the leachate from the precipitates formed in the cyanide-polysulfide reaction were below 3 mg/L.

It is recommended to apply technical grade sodium polysulfide, also called "zinc purifier", for pre-treatment of concentrated spent cyanide liquors. This recommendation is based mostly on the broad availability of this reagent, and on the fact that its use is associated with the formation of much smaller quantities of sludge than those generated with the application of calcium polysulfide.

DEVELOPMENT OF POLYSULFIDE TECHNOLOGY FOR TREATMENT OF CONCENTRATED SPENT CYANIDE LIQUORS

1.0 INTRODUCTION

Concentrated spent cyanide liquors are by-products of several different industrial processes. Although they are usually produced in relatively small quantities, their storage, transport, treatment, and disposal present considerable hazards and serious technological difficulties. Disposal of these concentrated cyanide-containing wastewaters poses considerable problems to the waste generator. Waste haulers are often reluctant to transport these wastes because of the difficulties and expense of final disposal. Transportation of these highly toxic wastewaters involves considerable risk, as leakage or rupture of the container would result in a potentially lethal situation. These disposal problems are of particular concern to operators of electroplating and metal finishing shops that are located in highly populated urban areas. Often, the concentrated cyanide-containing wastewaters remain stored in tanks and create a hazardous situation for employees in these shops. Sometimes these wastewaters are discharged in a clandestine fashion into the municipal sewer system, creating problems downstream.

Examples of industries that generate spent cyanide liquors are electroplating and metal finishing shops, and gold and

silver extraction operations. For reasons indicated above, concentrated cyanide solutions often accumulate in electroplating and metal finishing shops. These accumulations of 4.5 to 9.0 m³, which may be collected over a period of years, are generally of concentrations of 1 to 3% cyanide, although higher concentrations may occur.

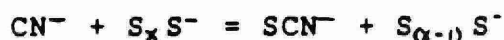
Considerable efforts have been devoted to the treatment of cyanide-containing wastewaters, and several treatment technologies have been developed. A well-known and commonly used treatment method for these wastewaters, particularly in the electroplating industry, is the alkaline-chlorination oxidation process which is practically applicable for wastewaters containing up to 500 mg/L CN. Other treatment processes include: peroxide oxidation, iron precipitation, ozonation with ultraviolet irradiation, carbon adsorption with catalytic oxidation, formaldehyde treatment, electrolytic oxidation, and catalytic SO₂ treatment.

Some of the common technologies available for the treatment of cyanide-containing wastewaters are not applicable to concentrated spent cyanide liquors. Other methods are associated with high capital and operating costs, or operational complexities that render them unsuitable for small industrial plants.

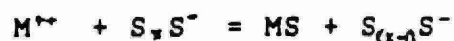
A relatively new technology available for detoxification of these concentrated spent cyanide liquors is that of polysulfide application (Ganczarczyk et al., 1985). Polysulfide-sulfur is commercially available in two forms: as limesulfur (calcium polysulfide) and as zinc purifier (sodium polysulfide). These products usually contain between 15% and 30% polysulfide-sulfur.

Polysulfide technology is based on the reaction between cyanide and polysulfide sulfur to form the much less toxic thiocyanate. Tests on the comparative toxicity of cyanide and thiocyanate (McKee and Wolf, 1963) showed that cyanide is two to three orders of magnitude more toxic than thiocyanate to trout, i.e. SCN^- is lethal to trout at 170 mg/L while CN^- is lethal at only 0.05 mg/L.

The reaction between cyanide and polysulfide can be simply expressed as:



Along with the conversion of cyanide to thiocyanate, polysulfide reacts with the metal-cyanide complexes and metal ions present to form metal sulfides which then precipitate out of solution. This reaction can similarly be represented as:



The required dosage of polysulfide-sulfur to convert cyanide to thiocyanate may be greater than stoichiometric requirements which

is a CN:poly-S^o ratio > 1:1.23 by weight.

2.0 PREVIOUS WORK

The reaction between cyanide and polysulfide-sulfur to form thiocyanate was used as early as 1896 to convert hydrogen cyanide in coke oven gas to thiocyanate. For cyanide solutions, the reaction was originally investigated by Wernlund and Zunick (1940). Luthy et al. (1977) and Luthy and Bruce (1979) studied such transformations in coke plant and coal gasification plant effluents. International Environmental Consultants (1979, 1981) investigated the use of the cyanide-polysulfide reaction for treatment of cyanide-containing wastewaters from the gold milling industry. However, no published data were available on the cyanide-polysulfide reaction in concentrated cyanide-containing wastewaters before the preliminary study by Takaoka and Ganczarczyk (1985). These experiments were conducted to investigate the cyanide-polysulfide reaction in a 2% (20,000 mg/L) solution of sodium cyanide. It was found that the reaction was not strongly affected by temperature, and proceeded rapidly both at room temperature and at 3°C). The reaction was 95% complete within one hour, and cyanide concentrations were non-detectable within two weeks at a CN:poly-S⁰ ratio of 1:2 (w/w).

In a follow-up research, Ganczarczyk et al. (1985) studied the reaction in two different cyanide-containing wastewater streams from an electroplating operation. One was a discharge from the first rinse tank in a copper and cadmium-plating

process, while the other was a stripper solution from the removal of spoiled metal plate. Initial cyanide concentrations ranged from 11,400 mg/L to 56,200 mg/L. In each case, rapid degradation of cyanide occurred; effective removal of cyanide within three days for the copper/cadmium-plating wastewater, and 99.9% cyanide removal within two days for the copper/nickel-plating wastewater.

3.0 SCOPE OF THE STUDY

This study is a continuation of the preliminary work done by Ganczarczyk et al. (1985) described earlier. The main objective of this investigation was to clarify some aspects of the previous experiments and to demonstrate that the polysulfide technology developed in the laboratory could be applied successfully on a larger scale. Three different concentrated spent liquors from a metal finishing shop were examined (zinc-plating, copper-plating and cadmium-plating spent cyanide liquors). Initially, tests were done on a laboratory scale to get an indication of the performance to be expected. Once satisfied that the reaction did proceed as expected, two pilot-scale tests were done. The culmination of this work will be a future full-scale application of polysulfide to treat a cadmium-plating spent cyanide liquor.

4.0 MATERIALS AND METHODS

4.1 Wastewater Streams Studied

In this project, the polysulfide technology was studied on the treatment of three different wastewater streams from a metal finishing shop: zinc-plating spent cyanide liquor, cadmium-plating spent cyanide liquor, and copper-plating spent cyanide liquor. The pH in all these liquors was greater than 12.0, while the cyanide concentrations ranged from 10,000 mg/L to 180,000 mg/L. In addition, a solution of potassium ferricyanide (20,000 mg/L CN) was also used to examine the effect of polysulfide on complexed cyanides.

4.2 Sources of Polysulfide

Polysulfide-sulfur from three sources were used in these experiments: limesulfur (calcium polysulfide), zinc purifier (sodium polysulfide), and calcium polysulfide produced in our laboratory from technical grade calcium oxide and sulfur. The limesulfur contained 230 g/L polysulfide-sulfur while the zinc purifier contained 150 g/L and the laboratory-produced polysulfide contained 200 g/L of polysulfide-sulfur. Wilson Laboratories produce limesulfur for use as an insecticide/fungicide (available at most nurseries), while Hanson Inc. produces zinc purifier.

4.3 Preliminary Laboratory Tests

Initially, laboratory experiments were conducted in one litre glass bottles sealed with rubber stoppers. Later pilot-scale tests were conducted on-site in open 50-gallon drums. Samples were taken from the reactors at regular intervals, preserved and then analyzed for total cyanide (CN), thiocyanate (SCN), and soluble metals (cadmium, chromium, copper, iron, nickel, and zinc) contents.

4.4 Sample Preservation

The standard procedures for sample preservation were adapted from those used by Luthy et al. (1979), Luthy and Bruce (1979), and International Environmental Consultants (1981). To obtain a sample for the determination of cyanide or thiocyanate, 20 mL of the reactor contents were transferred to a 200 mL volumetric flask, and diluted to the mark with distilled water. A few millilitres of a suspension of lead sub-acetate in water were added to the diluted samples to precipitate sulfides. Sodium hydroxide solution was added to the samples in measured quantities during the sulfide precipitation process to maintain a pH range of 10 to 11. The lead sulfide precipitate was immediately separated from the sample by vacuum filtration. The filtrate was collected and its pH increased to greater than 11.0 with sodium hydroxide solution. The treated samples were stored in the dark at 3°C.

4.5 Cyanide and Thiocyanate Determination

The method of cyanide determination was adapted from the method of Knechtel and Conn as cited by Conn (1981). This method is similar to the acid reflux/distillation method in "Standard Methods" (1980) with an argentometric titration finish. The method adopted for thiocyanate determination was based on mercuric titrimetry after Vogel (1960) using 0.1 N mercuric sulfate. An excess of iron alum (ferric ammonium sulfate) was added to the sample under acidic conditions to produce the characteristic deep red colour of ferric thiocyanate. After mercuric titration, the mercuric ion replaces the ferric ion and the red colour gradually disappears, leaving the solution colourless.

4.6 Polysulfide Determination

Polysulfides were determined with a procedure developed by Schulek as cited by Karchmer (1970). This method was based on the reaction of alkali cyanides with the soluble polysulfides in the absence of oxygen to form one thiocyanate ion for every atom of polysulfide-sulfur. The cyanide-polysulfide reaction was carried out in a boric acid medium. Hydrogen sulfide and excess hydrogen cyanide were driven off by boiling the acidified solution; the thiocyanate remained unaffected in solution.

4.7 Metals Analysis

The analysis for soluble metals was performed using an

atomic absorption spectrophotometer. A measured volume of sample (filtered by a 0.45 micron membrane filter) was boiled with 20 mL of concentrated nitric acid to decompose the residual cyanide that could interfere with the metals analysis. After cooling, the samples were subjected to atomic absorption spectrophotometry.

4.8 Determination of Heat of Reaction

The values of the heats of reaction were determined by measuring the temperature rise in the stoppered reaction vessel during the cyanide liquors-polysulfide reaction. In each case, 50 mL samples were used, and the reactor was continually agitated to ensure a uniform temperature distribution throughout the vessel.

4.9 Leaching Procedures

The procedure employed in the precipitate leaching tests was as follows: The precipitate was first dried in an oven at 103°C. One gram of the dried precipitate was added to 100 mL of distilled water. To some precipitate samples, one gram of flyash was added. All samples were then shaken, and leached metals concentrations were determined at regular intervals.

5.0 EXPERIMENTAL PROGRAM AND RESULTS

5.1 Comparison of Calcium Polysulfide and Sodium Polysulfide Effectiveness

The first set of experiments was designed so that the general effectiveness of calcium polysulfide and sodium polysulfide in the reaction with cyanide could be determined. A wastewater containing 64,900 mg/L of cyanide was reacted with both types of polysulfide at various cyanide to polysulfide ratios. The results are presented in Tables 1 and 2.

5.2 On-Site Production of Polysulfide

The main objective of the above tests was to determine whether or not on-site production of polysulfide would be feasible. Tests in the laboratory showed that calcium polysulfide could easily be produced in concentrations of 20% or more polysulfide sulfur (Table 12). Because the materials ie. calcium oxide and elemental sulfur, required for its production are relatively inexpensive, calcium polysulfide could be an even more attractive reagent if it could be shown that both types of polysulfides were equally effective.

5.3 Preliminary Tests on Plating Wastewaters

The second series of experiments involved the application of limesulfur to the three plating wastewaters on a small laboratory scale to determine optimum dosages for the best removal efficiencies. The reactions were carried out at CN:poly-S●

ratios of 1:1.5 and 1:2. The results are presented in Tables 3 to 8, and in Figures 1 to 6.

5.4 Effects of Dilution

It was also desired to determine the effect of dilution on the reaction between cyanide and polysulfide. Here, samples of the three wastewaters were diluted to two or three times their initial volume, and then reacted with calcium polysulfide at CN:poly-S²⁻ ratios of 1:1.5 and 1:2 (w/w). It was felt that a complete range of pollutant concentrations should be examined to ensure that the cyanide/polysulfide reaction proceeds as expected under a wide range of operating conditions, ie. the reaction is as effective on relatively diluted wastewaters as it is on very concentrated wastewaters. These dilution results are presented in Tables 9,10 and 11, and in Figures 7,8 and 9.

5.5 Heat of Reaction

Since the cyanide/polysulfide reaction is an exothermic one, it was necessary to determine the heat of reaction for the various plating-wastewater/polysulfide mixtures to ensure that no potentially hazardous situations could develop from the application of this technology. The cyanide concentrations in these tests were varied along with the amount of polysulfide added to see their effect on the heat of reaction. These results are shown on Table 13.

5.6 Leaching Tests

It was also of interest to note the leaching characteristics of the precipitates (sludge) formed in the cyanide/polysulfide reactions. A number of preliminary leaching tests were conducted to determine the amounts of heavy metals that could be released when the precipitates were shaken with water. Shake-tests were carried out using a wrist-action shaker. Although under Regulation 309 (Environmental Protection Act, June 1985) any sludge generated by an electroplater is considered hazardous (and hence subject to hazardous waste disposal), it was felt that the sludge formed in the cyanide/polysulfide reaction could be effectively immobilized and made acceptable for disposal at local secured landfills. The preliminary leaching results for the three sludges in this study are presented in Tables 14, 15 and 16. For some samples, flyash was added so that some indication as to the potential effectiveness of pozzolanic solidification could be obtained.

5.7 Removal of Residual Polysulfide

Because polysulfide was added in excess of stoichiometric requirements to the cyanide liquors (to enhance metal removal and complete the cyanide conversion), it was inevitable that some polysulfide would remain unused after completion of the reaction. Polysulfide is regarded as an active compound so it does have a potential to create pollution problems in receiving waters in the case of a direct discharge. Although this technology is

case of a direct discharge. Although this technology is primarily geared towards small metal finishing operations that may discharge the treated wastewater to municipal sewers, it was still felt that removal of the residual polysulfide should be studied. Therefore, some preliminary tests on the application of ferrous sulfate to remove residual polysulfide were performed, and their results are presented in Table 17.

5.8 Pilot-Scale Tests

The final series of experiments concerned the pilot-scale application of this technology. It was necessary to show that the cyanide treatment method developed could be successfully applied on-site under the realistic conditions found outside of the laboratory. One test involved the application of 20 litres of calcium polysulfide produced in the laboratory of the University of Toronto to 110 litres of a zinc-plating spent cyanide liquor to achieve an initial CN:poly-S[●] ratio of 1:2. The initial cyanide concentration was 17,900 mg/L and the polysulfide contained over 200 g/L of polysulfide-sulfur. The other pilot-scale test involved the addition of 61 litres of zinc purifier (150 g/L polysulfide-sulfur) to 25 litres of a cadmium-plating spent cyanide liquor. The initial cyanide concentration was 181,000 mg/L and the resulting CN:poly-S[●] ratio was 1:2. The results of the two pilot-scale tests are presented in Tables 18 and 19, and in Figures 10 and 11.

5.9 Iron-Cyanide Complexes

In the course of this investigation, it was postulated that the presence of iron-cyanide complexes may limit or hinder the effectiveness of polysulfide technology. It has been shown previously (Luthy and Bruce, 1978) that polysulfide does not react with ferricyanide to form thiocyanate. Some of the wastewaters dealt with in this study had significant amounts of both iron and cyanide, so a supplemental series of experiments on solutions of potassium ferricyanide was conducted. Varying amounts of sodium polysulfide were added to a solution of potassium ferricyanide to obtain CN:poly-S⁰ ratios of 1:1.5, 1:2 and 1:2.5. The results of these tests are presented in Table 20.

Table 1: Decrease of Cyanide Concentrations (mg/L) with the Application of Calcium Polysulfide

Ratio Of CN:poly-S ^a (w/w)	DURATION OF EXPERIMENTS					
	0	0.5 hr	1 day	2 day	3 day	4 day
1:1	64900	2125.0	2200.0	2437.5	2412.5	2050.0
1:1.5	64900	125.0	75.0	12.5	25.0	0.0
1:2	64900	12.5	12.5	0.0	0.0	0.0

Table 2: Decrease of Cyanide Concentrations (mg/L) with the Application of Sodium Polysulfide

Ratio Of CN:poly-S ^a (w/w)	DURATION OF EXPERIMENTS					
	0	0.5 hr	1 day	2 day	3 day	4 day
1:1	64900	2850.0	2675.0	2400.0	2125.0	2125.0
1:1.5	64900	100.0	500.0	137.5	25.0	25.0
1:2	64900	50.0	75.0	0.0	0.0	0.0

Table 3: Effects of Cadmium-Plating Spent Liquor Treatment
(CN:poly-S^o Ratio of 1:1.5)

Pollutants in Solution (mg/L)	DURATION OF THE EXPERIMENTS					
	Initial	1 day	7 day	14 day	21 day	28 day
CN	65750.0	62.5	31.2	0.0	0.0	0.0
Fe	704.8	605.0	677.0	625.0	642.0	392.7
Zn	217.5	7.5	4.0	7.8	9.8	4.0
Cu	287.5	111.2	41.5	21.5	27.0	15.0
Ni	28.3	n.d.	5.0	n.d.	6.5	n.d.
Cd	4212.5	5.0	2.9	6.0	4.4	3.5
Cr	24.8	2.2	1.5	2.0	1.5	1.5

Note: n.d. = not done

Table 4: Effects of Cadmium-Plating Spent Liquor Treatment
(CN:poly-S^o Ratio of 1:2)

Pollutants in Solution (mg/L)	DURATION OF THE EXPERIMENTS					
	Initial	1 day	7 day	14 day	21 day	28 day
CN	65750.0	62.5	0.0	0.0	0.0	0.0
Fe	704.8	631.5	660.7	648.7	678.0	357.4
Zn	217.5	10.5	4.0	5.6	5.6	4.0
Cu	287.5	95.7	23.2	9.3	14.2	12.7
Ni	28.3	5.5	4.5	7.1	5.5	4.5
Cd	4212.5	4.5	4.7	4.0	5.3	3.2
Cr	24.8	3.0	1.0	1.3	0.5	0.5

Table 5: Effects of Copper-Plating Spent Liquor Treatment
(CN:poly-S^o Ratio of 1:1.5)

Pollutants in Solution (mg/L)	DURATION OF THE EXPERIMENTS					
	Initial	1 day	7 day	14 day	21 day	28 day
CN	56075.0	125.0	93.8	0.0	0.0	0.0
Fe	416.2	466.7	450.0	382.0	435.0	275.0
Zn	2.5	0.5	0.0	2.0	1.0	1.5
Cu	35050.0	117.0	138.5	125.5	109.0	36.0
Ni	5.5	2.0	1.5	0.4	1.8	0.8
Cd	0.5	0.5	0.2	0.2	0.0	0.0
Cr	2.0	1.7	0.5	0.7	0.0	0.0

Table 6: Effects of Copper-Plating Spent Liquor Treatment
(CN:poly-S^o Ratio of 1:2)

Pollutants in Solution (mg/L)	DURATION OF THE EXPERIMENTS					
	Initial	1 day	7 day	14 day	21 day	28 day
CN	56075.0	62.5	0.0	0.0	0.0	0.0
Fe	416.2	485.0	396.0	452.0	425.0	356.0
Zn	2.5	0.7	0.0	0.0	0.5	1.0
Cu	35050.0	131.0	49.0	37.5	42.0	10.1
Ni	5.5	1.4	0.8	1.2	0.6	0.6
Cd	0.5	0.5	0.3	0.0	0.0	0.0
Cr	2.0	1.5	1.0	1.2	0.7	0.0

Table 7: Effects of Zinc-Plating Spent Liquor Treatment
(CN:poly-S^o Ratio of 1:1.5)

Pollutants in Solution (mg/L)	DURATION OF THE EXPERIMENTS					
	Initial	1 day	7 day	14 day	21 day	28 day
CN	7900.0	187.5	125.0	0.0	0.0	0.0
Fe	855.0	634.0	565.0	670.0	710.0	680.0
Zn	5325.0	191.8	174.0	182.2	214.0	187.5
Cu	6.5	3.5	0.5	0.0	0.7	0.5
Ni	2.5	1.0	0.8	1.1	0.6	0.8
Cd	0.5	0.5	0.3	0.0	0.0	0.0
Cr	4.5	2.2	0.7	1.2	0.7	0.0

Table 8: Effects of Zinc-Plating Spent Liquor Treatment
(CN:poly-S^o Ratio of 1:2)

Pollutants in Solution (mg/L)	DURATION OF THE EXPERIMENTS					
	Initial	1 day	7 day	14 day	21 day	28 day
CN	7900.0	175.0	125.0	0.0	0.0	0.0
Fe	855.0	651.0	509.0	656.0	704.0	571.0
Zn	5325.0	132.0	2.5	3.0	1.8	2.1
Cu	6.5	2.7	0.5	0.0	0.3	0.5
Ni	2.5	0.8	0.4	0.6	0.4	0.4
Cd	0.5	0.3	0.3	0.0	0.0	0.0
Cr	4.5	2.2	0.5	0.7	0.0	0.0

Table 9: Effect of Dilution on the Treatment of
Cadmium-Plating Spent Liquor

Ratio Of CN:poly-S ⁹ (w/w)	DURATION OF EXPERIMENTS				
	Initial	1 day	4 days	7 days	14 days
1:1.5	65750.0	62.5	n.d.	31.2	0.0
1:2	65750.0	62.5	n.d.	0.0	0.0
1:2	21600.0	250.0	0.0	0.0	0.0
1:2	6187.5	62.5	31.0	0.0	0.0

Note: n.d. = not done

Table 10: Effect of Dilution on the Treatment of
Copper-Plating Spent Liquor

Ratio Of CN:poly-S ⁹ (w/w)	DURATION OF EXPERIMENTS				
	Initial	1 day	4 days	7 days	14 days
1:1.5	56075.0	125.0	n.d.	93.8	0.0
1:2	56075.0	62.5	n.d.	0.0	0.0
1:2	23650.0	250.0	31.3	0.0	0.0
1:2	5687.5	62.5	0.0	0.0	0.0

Note: n.d. = not done

Table 11: Effect of Dilution on the Treatment of Zinc-Plating Spent Liquor

Ratio Of CN:poly-S ₂ (w/w)	DURATION OF EXPERIMENTS				
	Initial	1 day	4 days	7 days	14 days
1:1.5	7900.0	187.5	125.0	0.0	0.0
1:2	7900.0	175.0	125.0	0.0	0.0
1:1.5	3625.0	125.0	62.5	31.3	0.0
1:2	3625.0	125.0	96.2	31.3	0.0

Table 12: Calcium Polysulfide Production

Sample	Components			Reaction Time (hrs)	Final Volume (mL)	Polysulfide Content (%)
	CaO (g)	S (g)	water (mL)			
1	20	70	300	24*	300	4-6
2	20	60	200	4	55	21-23
3	20	70	200	4-5	96	22-24
4	30	70	300	5	127	8-10
5	20	60	400	7	130	15-17

- Notes: 1. Asterisk indicates use of reflux condenser
2. All samples were stirred throughout boiling time with a magnetic stirrer

Table 13: Estimation of Reaction Heat

Sample Source	Cyanide Amount (g)	Initial CN:poly-S ^o ratio	Maximum Temp. Rise (°C)	Heat of Reaction cal/g CN
Zinc-Plating Solution	0.3500	1:1.5	2.87	410.0
		1:2	2.97	424.3
Cadmium-Plating Solution	0.6103	1:1.5	4.97	407.2
		1:2	5.16	422.7
Copper-Plating Solution	1.1719	1:1.5	5.12	218.4
		1:2	5.34	227.8
Copper-Plating Solution	0.9354	1:1.5	3.50	187.1
	2.8013		9.50	169.6
KCN Solution	0.2000	1:2	1.66	415.0
			1.72	430.0

Note: Specific heat of these solutions is assumed to be 1 cal/g · °C

Table 14: Metal Ion Concentrations in the Leachate from the Cadmium-Plating Spent Liquor Treatment Sludge (mg/L)

Pollutant in Solution		Duration of Leaching		
		1 day	3 days	9 days
Fe	A	9.6	6.8	6.6
	B	6.0	4.6	4.0
Zn	A	0.2	0.0	0.0
	B	0.2	0.0	0.0
Cu	A	0.8	1.0	0.8
	B	0.8	1.0	0.8
Ni	A	0.6	0.0	0.4
	B	0.8	0.2	0.6
Cd	A	0.0	0.0	0.0
	B	0.2	0.0	0.0
Cr	A	0.0	0.0	0.0
	B	0.0	0.0	0.0

Note: 'A' represents sample + flyash
'B' represents sample only

Table 15: Metal Ion Concentrations in the Leachate from the Copper-Plating Spent Liquor Treatment Sludge (mg/L)

Pollutant in Solution		Duration of Leaching		
		1 day	3 days	9 days
Fe	A	0.6	0.0	0.8
	B	0.2	0.2	0.8
Zn	A	0.2	0.4	0.4
	B	0.2	0.2	0.2
Cu	A	2.6	2.0	0.6
	B	1.0	1.0	0.8
Ni	A	0.4	0.2	0.2
	B	0.4	0.4	0.0
Cd	A	0.0	0.0	0.0
	B	0.0	0.0	0.0
Cr	A	0.0	0.0	0.0
	B	0.0	0.0	0.0

Note: 'A' represents sample + flyash
'B' represents sample only

Table 16: Metal Ion Concentrations in the Leachate from the Zinc-Plating Spent Liquor Treatment Sludge (mg/L)

Pollutant in Solution		Duration of Leaching			
		3 days	7 days	9 days	15 days
Fe	A	n.d.	14.0	6.8	13.0
	B	n.d.	11.6	4.6	11.2
Zn	A	0.0	0.2	0.0	0.0
	B	6.6	5.1	0.0	4.8
Cu	A	n.d.	0.8	1.0	0.8
	B	n.d.	0.6	1.0	0.6
Ni	A	n.d.	0.4	0.0	0.0
	B	n.d.	0.2	0.2	0.0
Cd	A	n.d.	0.0	0.0	0.0
	B	n.d.	0.0	0.0	0.0
Cr	A	n.d.	0.0	0.0	0.0
	B	n.d.	0.0	0.0	0.0

Note: 'A' represents the sample + flyash
'B' represents the sample only
'n.d.' = not done

Table 17: Removal of Residual Polysulfide from the Cadmium-Plating Solution

Test No.	1	2	3	4	5
Volume of Sample (mL)	10	10	10	10	10
Volume of 10% Ferrous Sulfate Solution Added (mL)	0	1	3	4	5
Polysulfide Concentration (mg/L)	10740.1	4618.2	961.8	480.9	705.3
Removal Efficiency (%)	0	43	91	96	93

Table 18: Effects of Zinc-Plating Spent Liquor Treatment
(Pilot-Scale Test #1; CN:poly-S^O =1:2)

Soluble Pollutants (mg/L)	DURATION OF THE EXPERIMENTS						
	Initial	1 day	3 day	6 day	13 day	23 day	30 day
CN	17900.0	1125.0	425.0	225.0	100.0	300.0	350.0
Fe	2600.0	220.0	140.0	100.0	120.0	120.0	120.0
Zn	9000.0	140.0	540.0	20.0	20.0	20.0	16.0
Cu	50.0	8.0	10.0	6.0	4.0	2.0	0.0
Ni	20.0	12.0	20.0	14.0	2.0	2.0	2.0
Cd	0.3	0.0	0.0	0.0	0.0	0.0	0.0
Cr	5.0	5.0	4.0	2.0	2.0	2.0	2.0
SCN	0	21140	12550	11620	4650	11620	6970

Table 19: Effects of Cadmium-Plating Spent Liquor Treatment
(Pilot-Scale Test #2; CN:poly-S^O = 1:2)

Soluble Pollutants (mg/L)	DURATION OF THE EXPERIMENTS					
	Initial	1 day	3 day	6 day	9 day	16 day
CN	181000.0	63.0	10.0	15.0	12.5	10.0
Fe	1400.0	6.2	2.5	0.8	2.0	1.9
Zn	940.0	0.6	0.6	0.7	2.0	0.8
Cu	660.0	0.8	1.0	1.1	1.2	0.6
Ni	36.0	3.8	3.0	2.4	1.8	1.4
Cd	9800.3	0.4	0.3	0.5	0.4	0.3
Cr	15.0	2.0	3.1	2.4	2.8	1.6
SCN	0	6970	3950	1160	2556	860

Table 20: Effects of Potassium Ferricyanide
Solution Treatment

No.	CN:poly-S ^o Ratio (w/w)	Soluble Pollutants (mg/L)	Duration of Experiments (days)			
			0	1	3	9
1	1:1.5	CN	20000	12000	10200	7750
		Fe	7155	3000	1800	1000
		SCN	0	0	0	0
2	1:2	CN	20000	7800	5000	8750
		Fe	7155	800	600	1400
		SCN	0	0	0	0
3	1:2.5	CN	20000	9500	1700	2250
		Fe	7155	1000	800	400
		SCN	0	0	0	0
4	1:2	CN	200	163	n.d.	125
		Fe	72	26	n.d.	20
		SCN	0	0	n.d.	0

Note: n.d. = not done

Table 21: Leachate Analysis of Sludges Resulting from Polysulfide Treatment of Cyanide Wastewaters

Pollutant in Solution	Max Conc'n Allowed*	Maximum Leachate Concentrations (mg/L)		
		Zn-plating	Cu-plating	Cd-plating
Fe	50.0	14.0	0.8	9.6
Zn	5.0	6.6 (0.2)	0.4	0.2
Cu	5.0	1.0	2.6	1.0
Ni	5.0	0.4	0.4	0.8
Cd	2.0	0.0	0.0	0.2
Cr	5.0	0.0	0.0	0.0

- Notes: 1. Bracketed value indicates that flyash was added
2. Asterisk indicates Metropolitan Toronto sewer-use by-laws

Table 22: Comparison of Pilot-Scale Applications of Polysulfide Technology

Pollutants in Solution	Max Conc'n Allowed*	Residual Concentration in Solution (mg/L)	
		Pilot-Scale #1	Pilot-Scale #2
Fe	50.0	120.0	1.9
Zn	5.0	16.0	0.8
Cu	5.0	0.0	0.6
Ni	5.0	2.0	1.4
Cd	2.0	0.0	0.3
Cr	5.0	2.0	1.6
CN	2.0	350.0	10.0

- Note: 1. Asterisk indicates Metropolitan Toronto sewer-use by-laws
2. Pilot-Scale #1 = Zinc-plating wastewater treatment
3. Pilot-Scale #2 = Cadmium-plating wastewater treatment

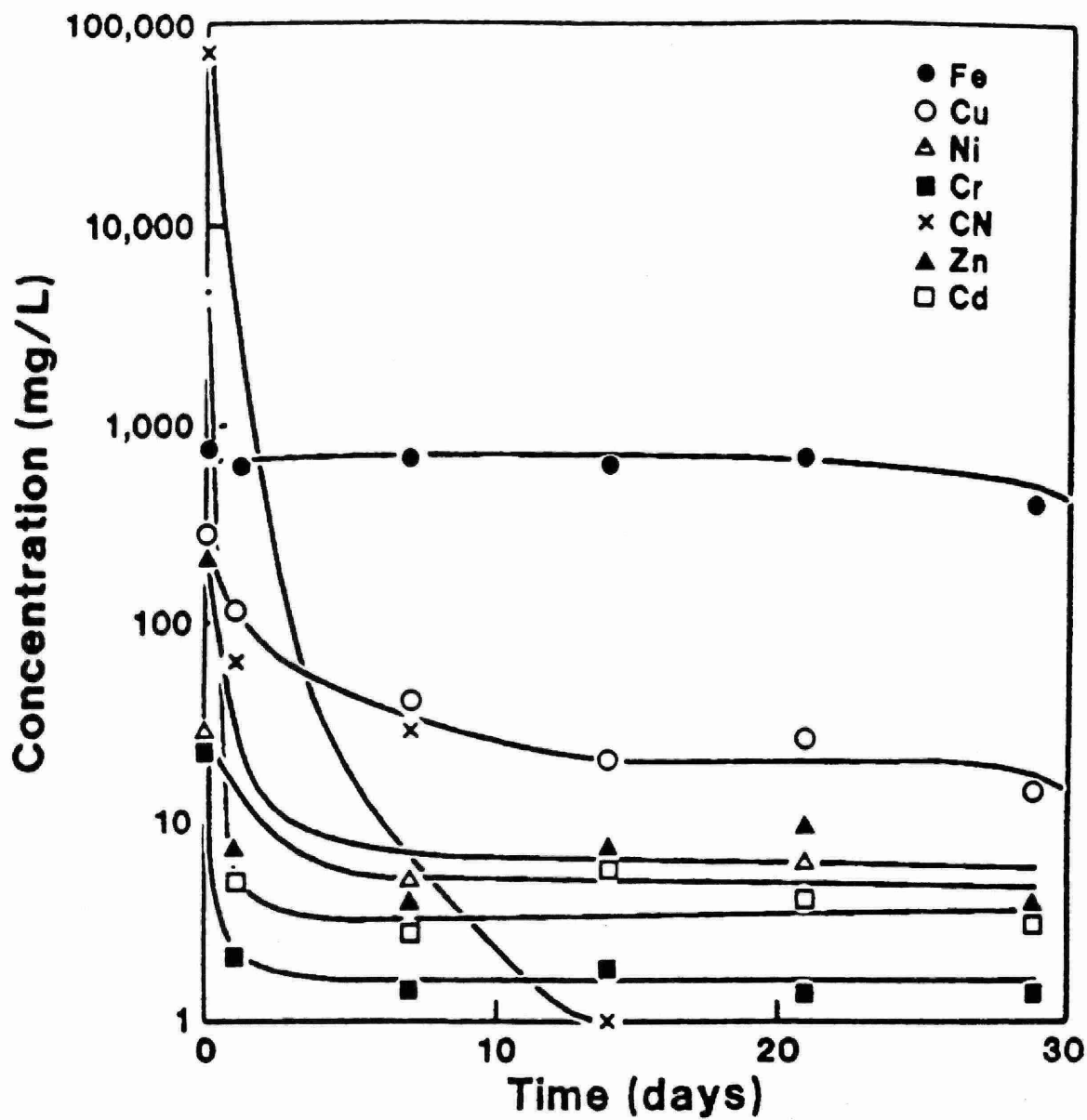


Figure 1: Effect of Calcium Polysulfide Treatment of Cadmium-Plating Spent Cyanide Liquor at the CN:poly-S⁰ Ratio of 1:1.5

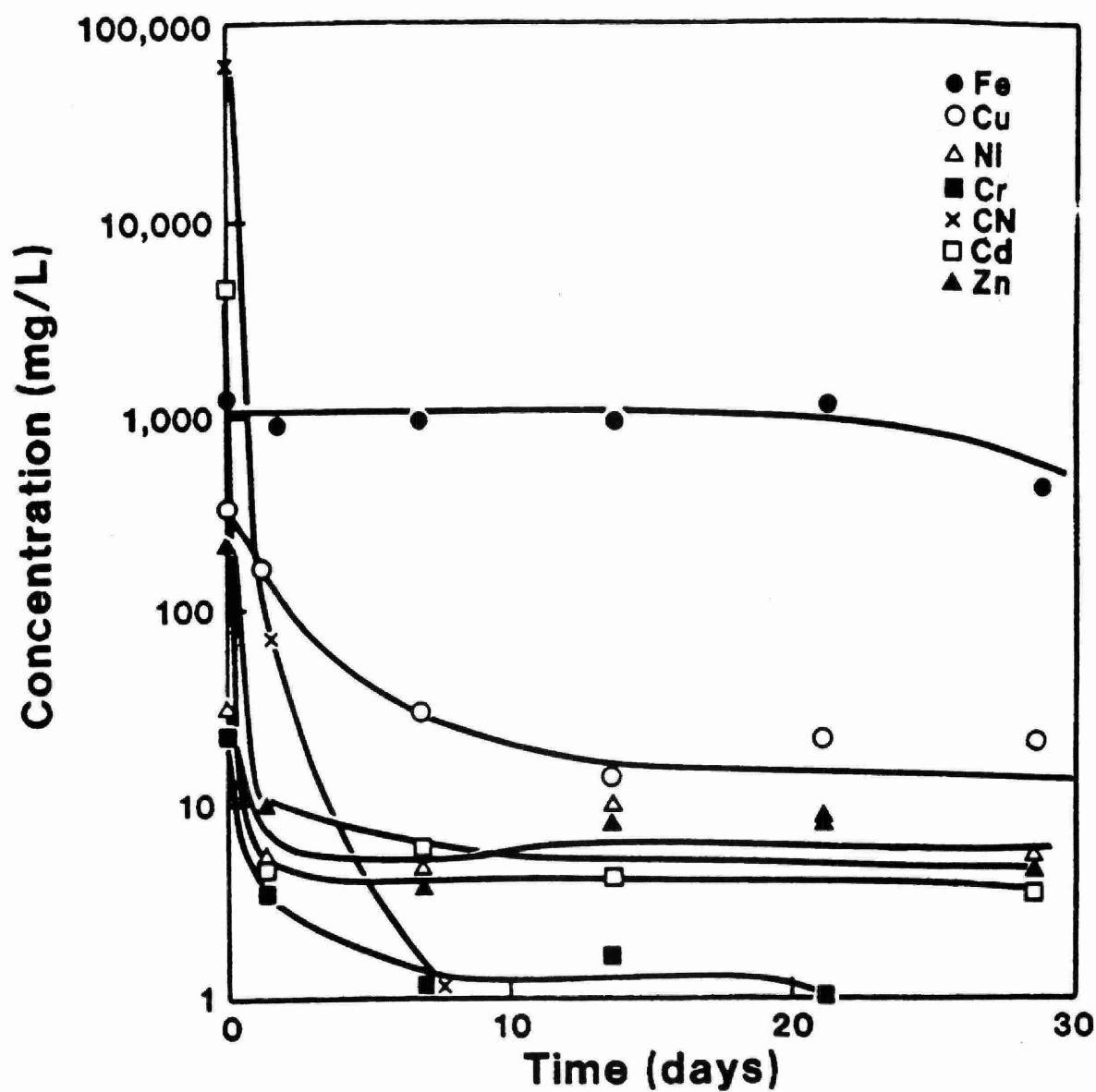


Figure 2: Effect of Calcium Polysulfide Treatment of Cadmium-Plating Spent Cyanide Liquor at the CN:poly-S⁰ Ratio of 1:2

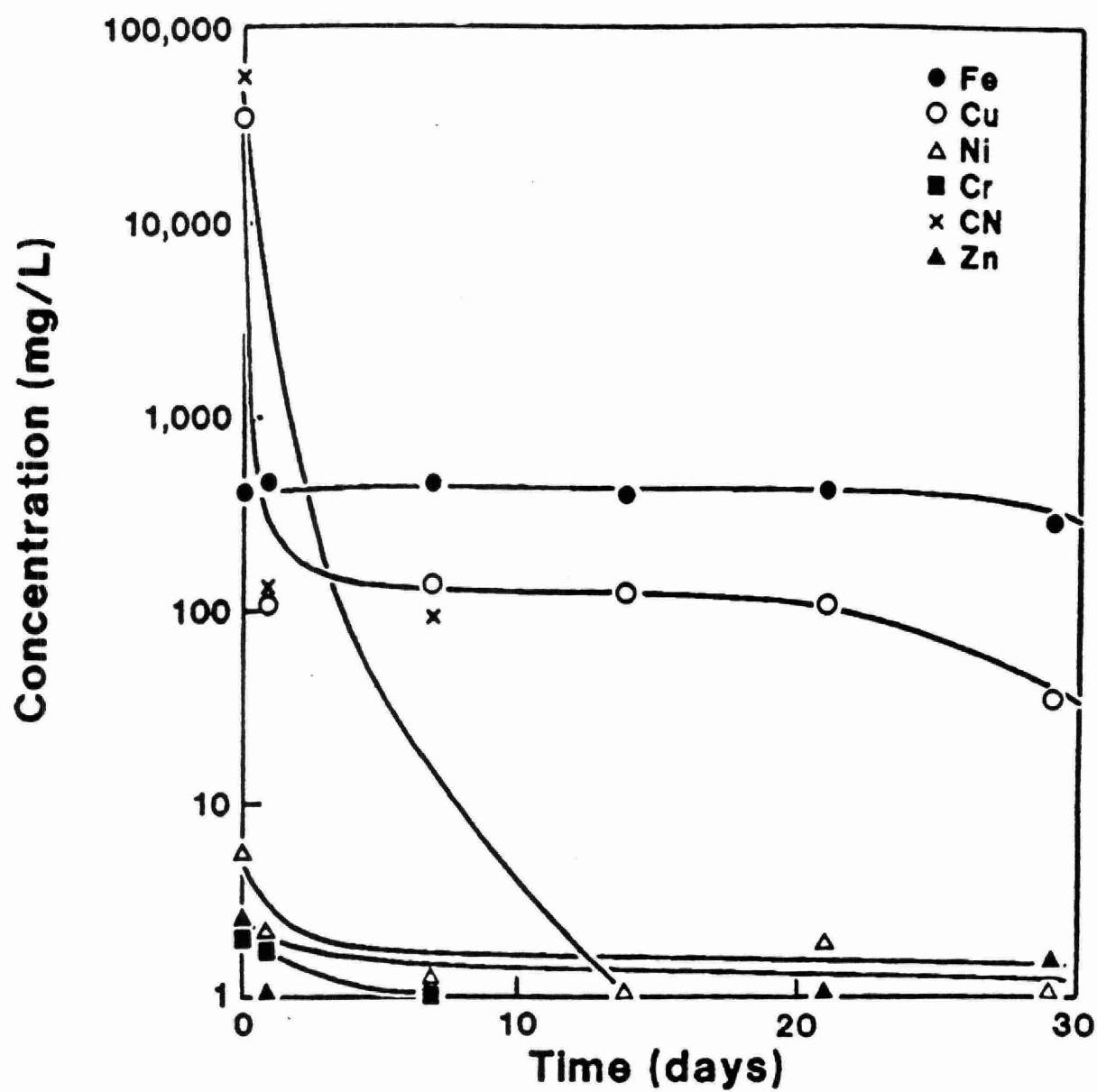


Figure 3: Effect of Calcium Polysulfide Treatment of Copper-Plating Spent Cyanide Liquor at the CN:poly-S^o Ratio of 1:1.5

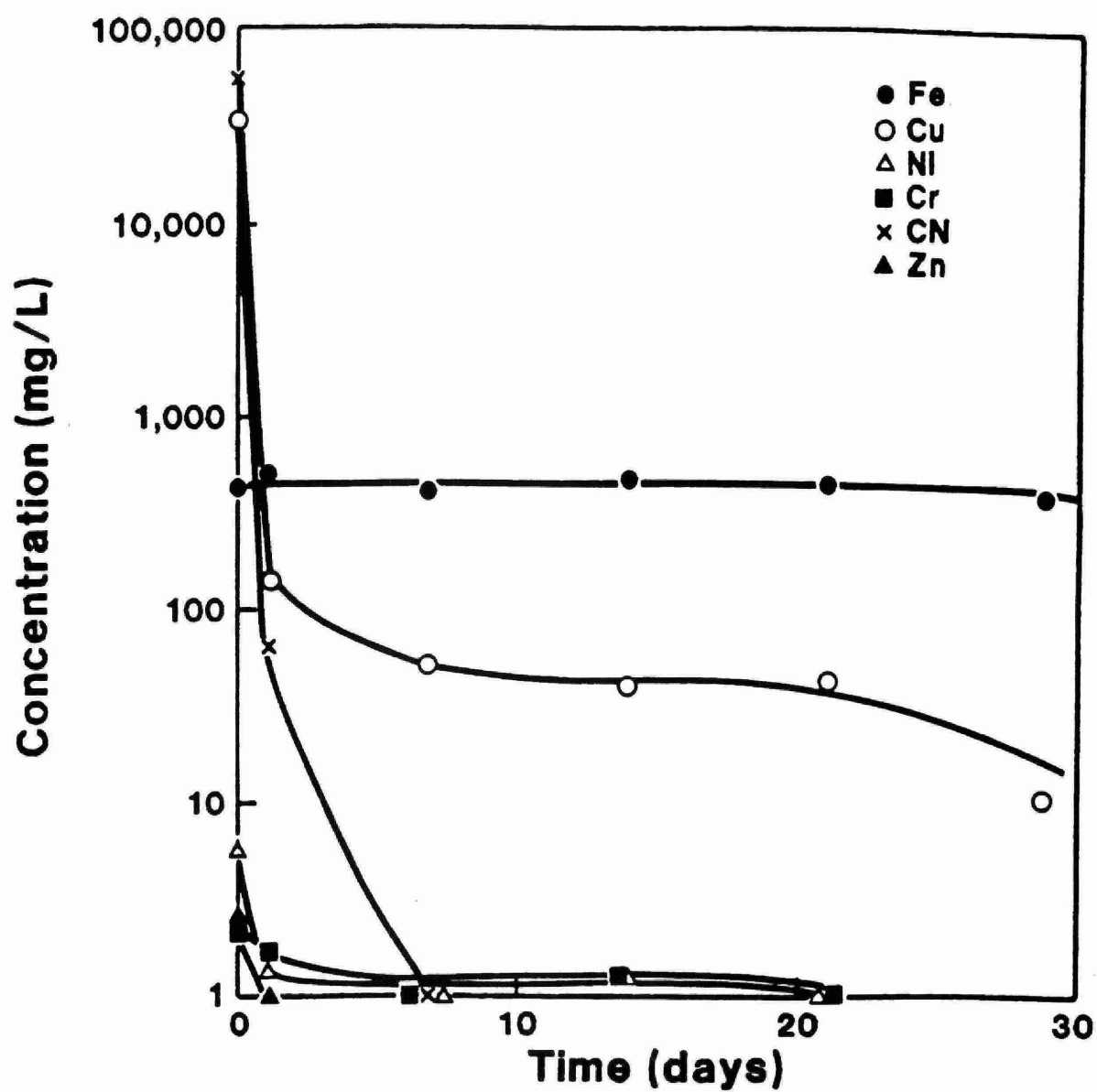


Figure 4: Effect of Calcium Polysulfide Treatment of Copper-Plating Spent Cyanide Liquor at the CN:poly-S^o Ratio of 1:2

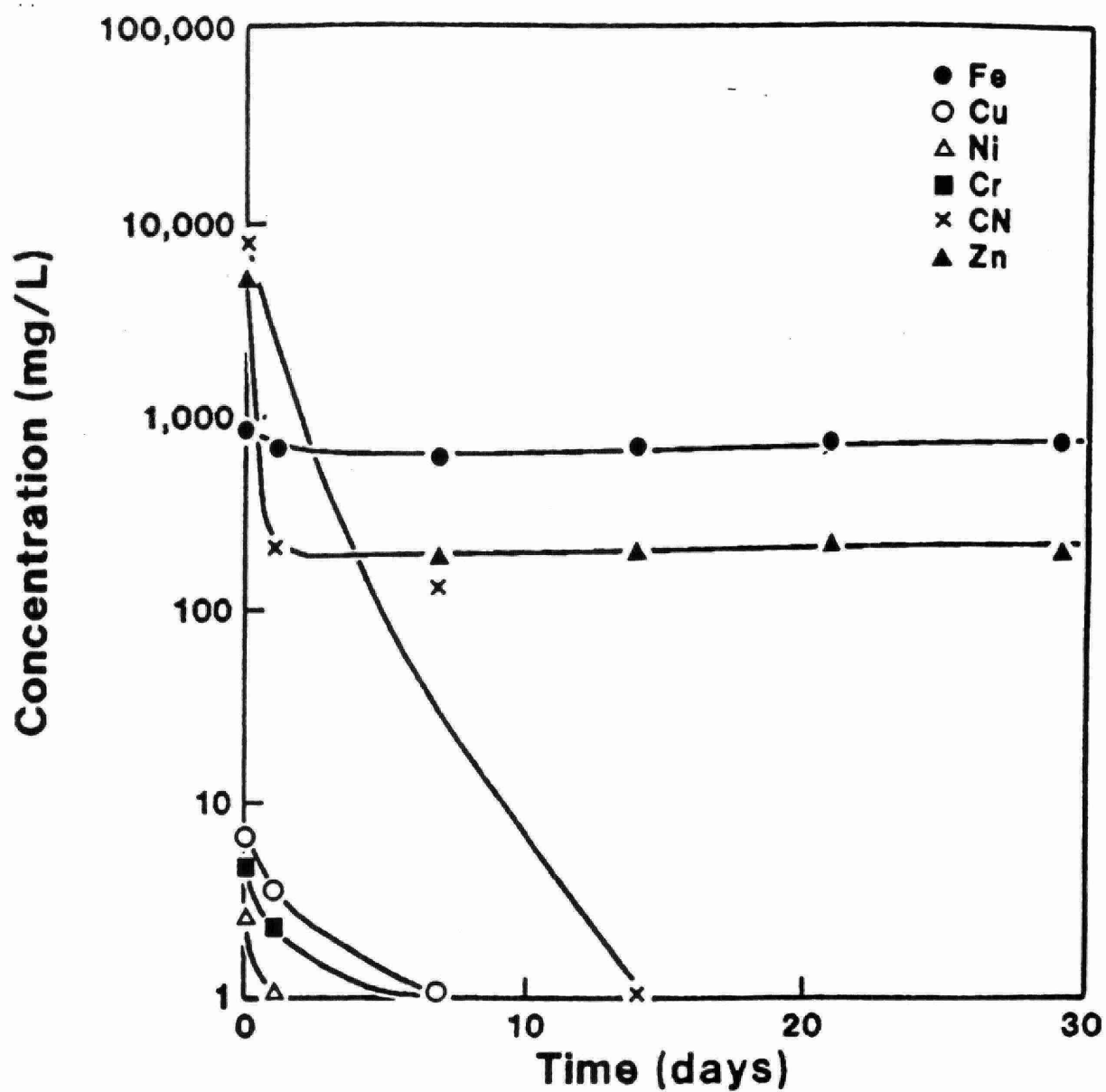


Figure 5: Effect of Calcium Polysulfide Treatment of Zinc-Plating Spent Cyanide Liquor at the CN:poly-S²⁻ Ratio of 1:1.5

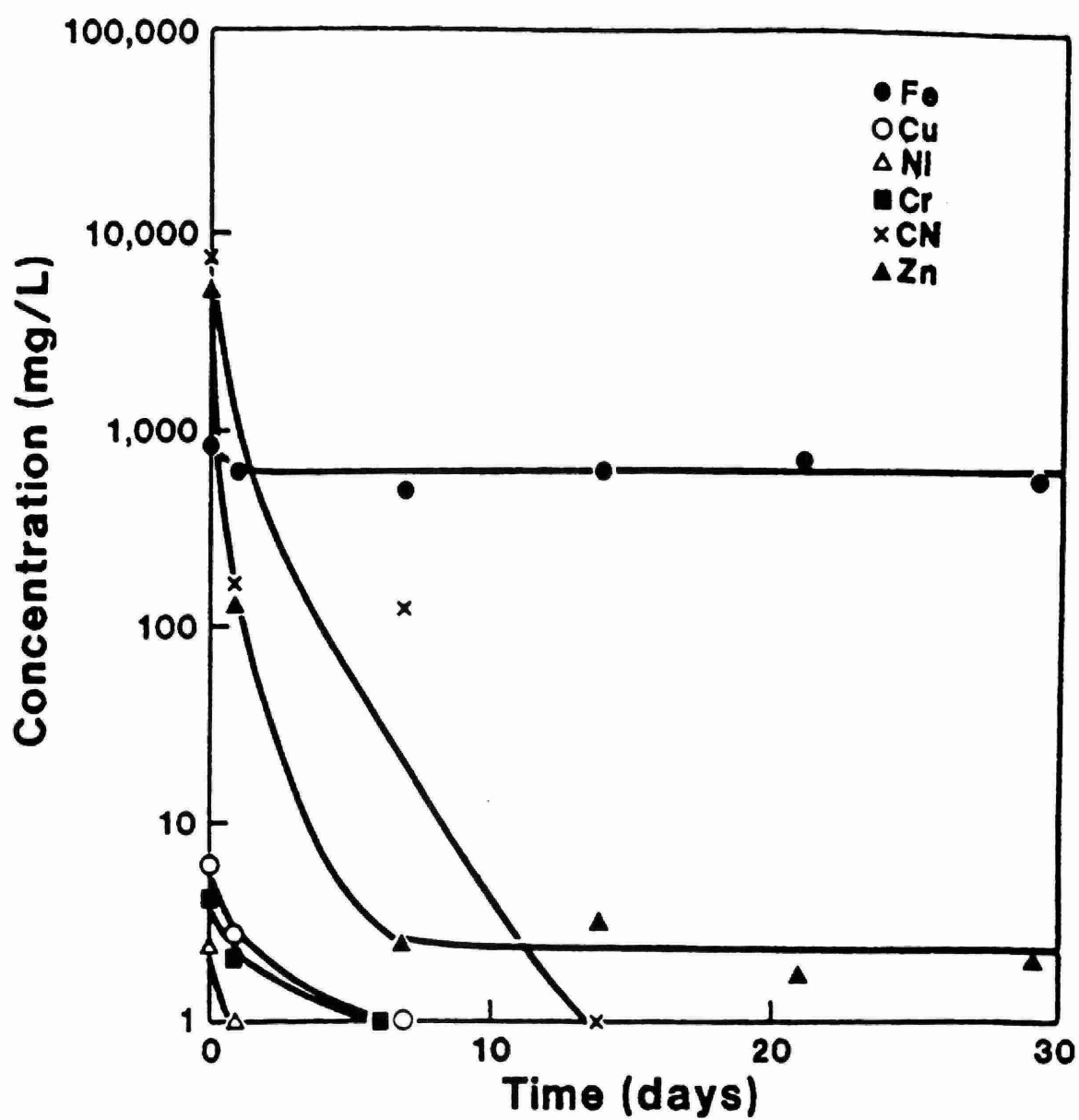


Figure 6: Effect of Calcium Polysulfide Treatment of Zinc-Plating Spent Cyanide Liquor at the CN:poly-S⁰ Ratio of 1:2

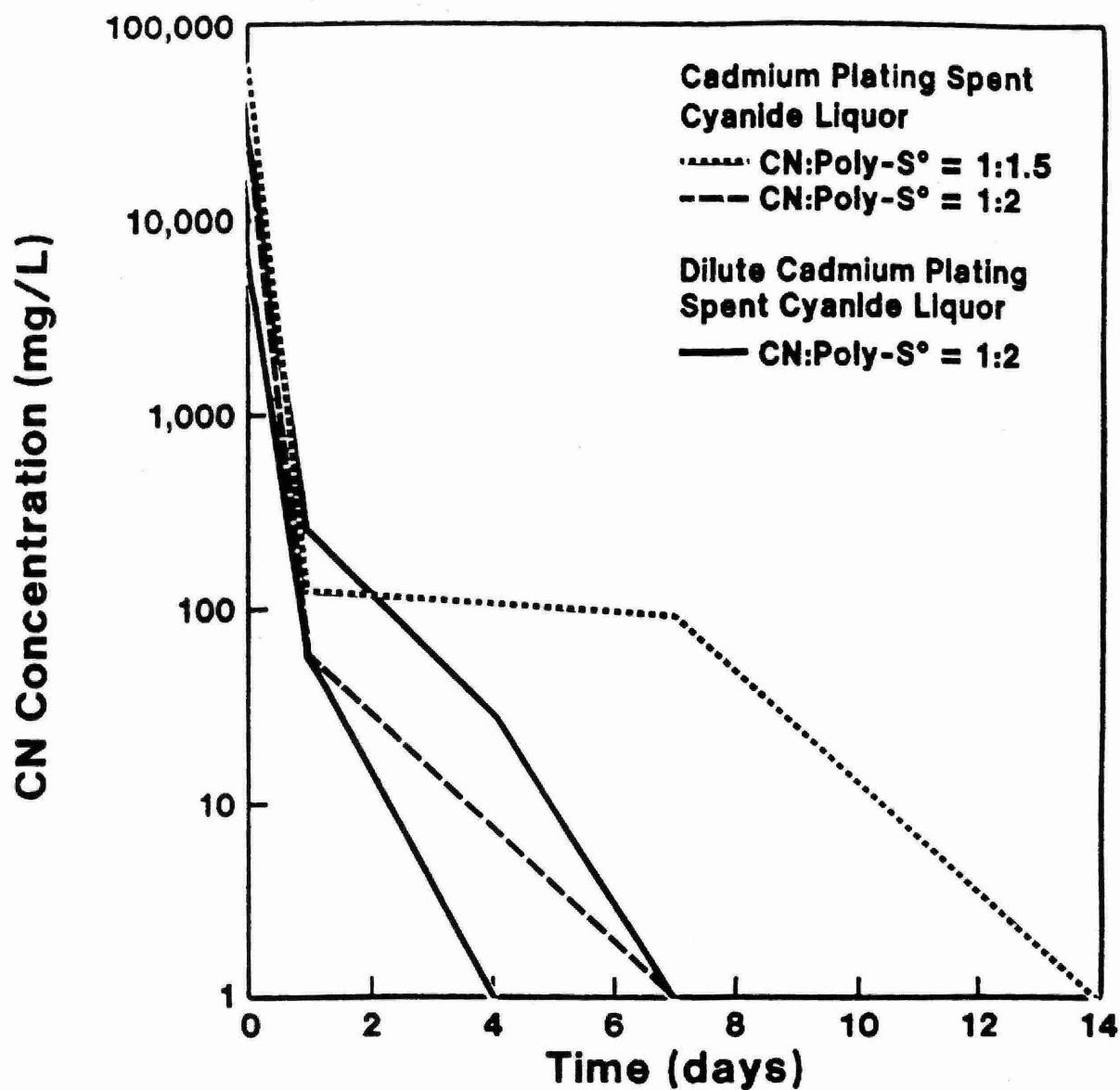


Figure 7: Effect of Dilution on Polysulfide Treatment of Cadmium-Plating Spent Cyanide Liquor

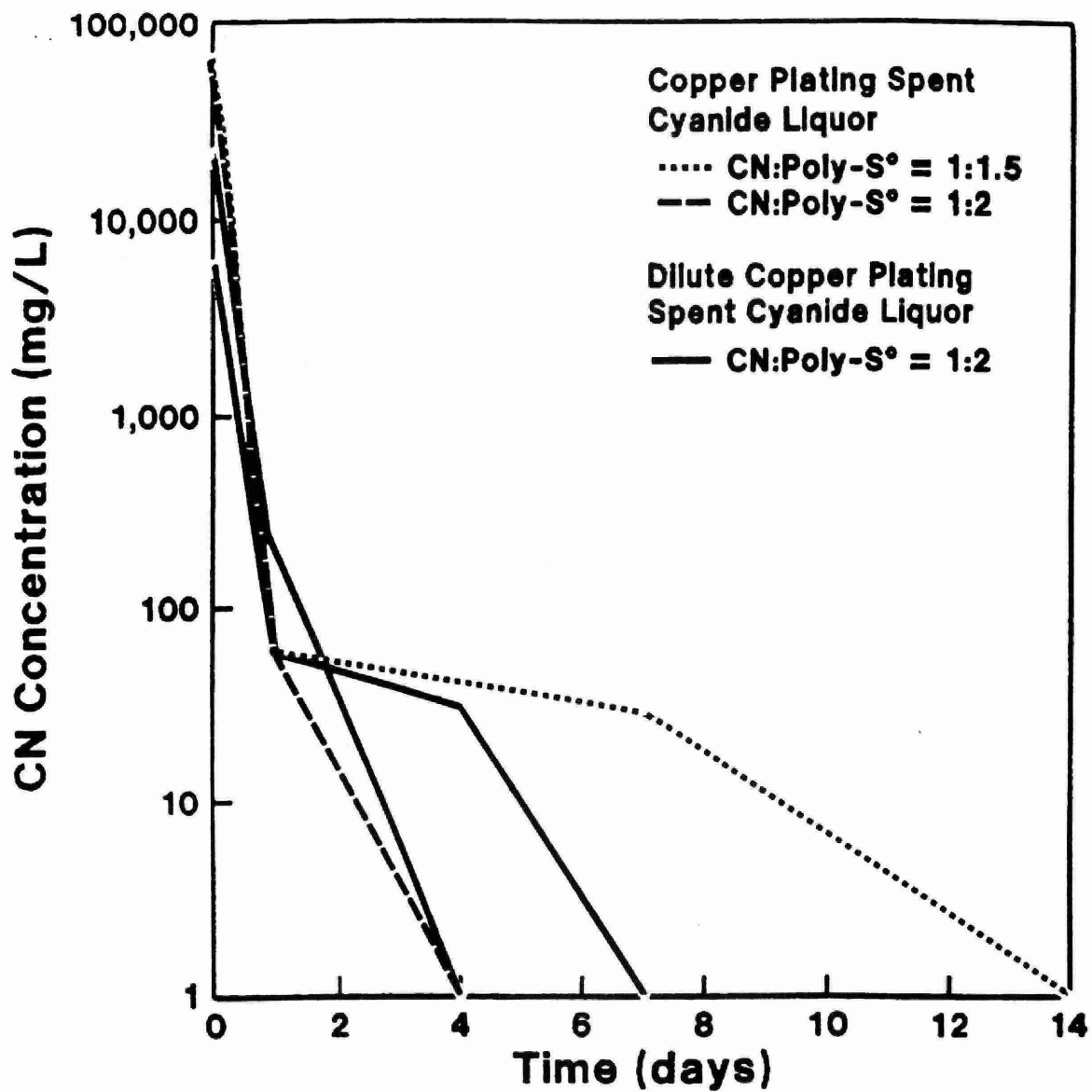


Figure 8: Effect of Dilution on Polysulfide Treatment of Copper-Plating Spent Cyanide Liquor

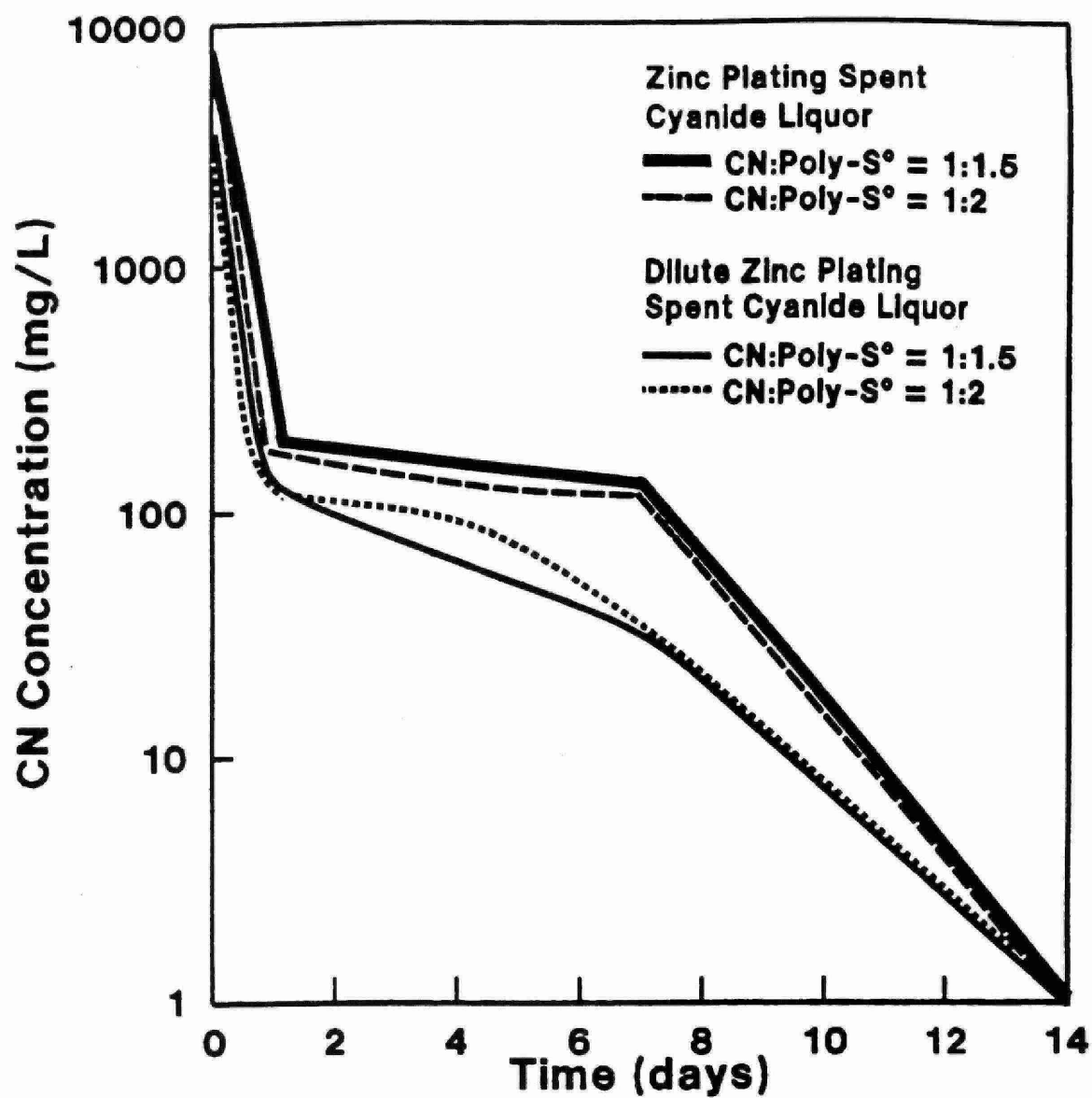


Figure 9: Effect of Dilution on Polysulfide Treatment of Zinc-Plating Spent Cyanide Liquor

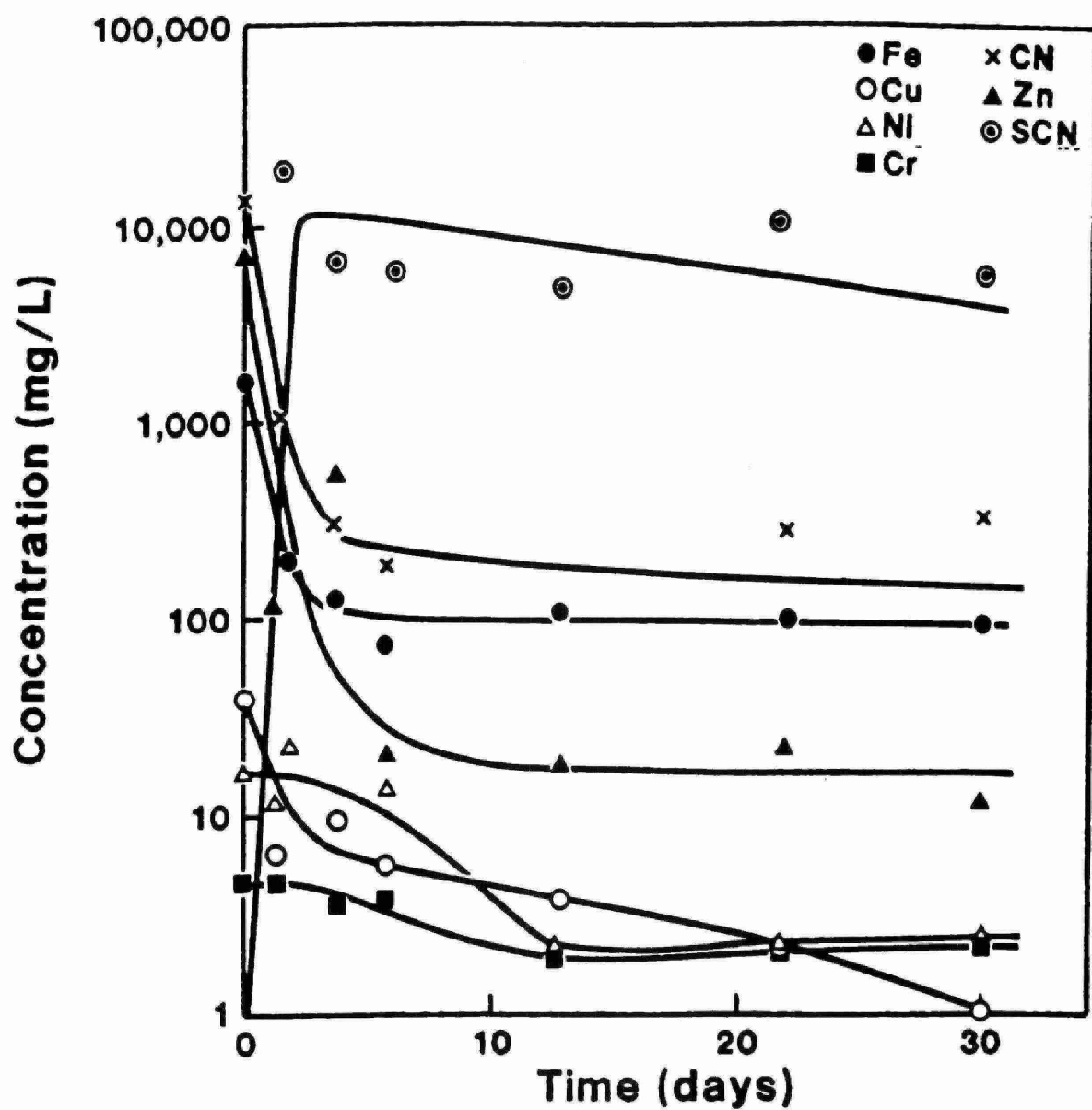


Figure 10: Pilot-Scale Calcium Polysulfide (laboratory produced) Treatment of Zinc-Plating Spent Cyanide Liquor at the CN:poly-S^o Ratio of 1:2

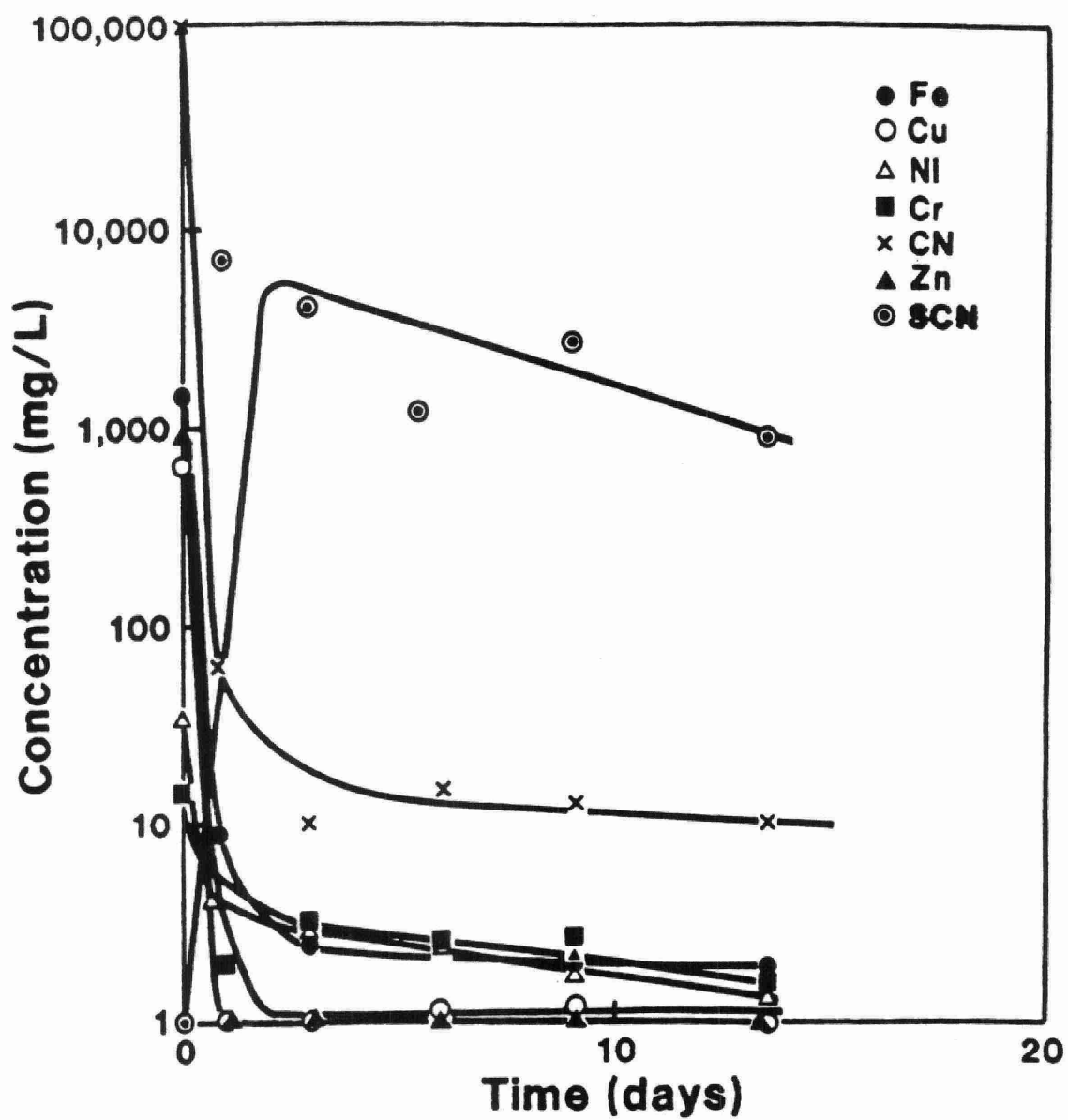


Figure 11: Pilot-Scale Sodium Polysulfide Treatment of Cadmium-Plating Spent Cyanide Liquor at the CN:poly-S⁰ Ratio of 1:2

6.0 DISCUSSION

6.1 Calcium Polysulfide vs Sodium Polysulfide

There were no significant treatment differences between the application of calcium polysulfide or sodium polysulfide for cyanide liquors treatment. Both types of polysulfide were effective in reducing cyanide concentrations at CN:poly-S⁰ ratios of 1:1.5 and 1:2 (Tables 1 and 2). Cyanide concentrations were reduced to non-detectable levels after only two days reaction time with the application of either polysulfide at the CN:poly-S⁰ ratio of 1:2. At the lower polysulfide dosage (CN:poly-S⁰=1:1), there was cyanide left in solution after four days. This was expected, however, because stoichiometric requirements are a CN:poly-S⁰ ratio of 1:1.23 (w/w).

6.2 Economic Aspects of Polysulfide Technology

Because calcium polysulfide could be shown to be less expensive if produced in bulk quantities, it was chosen as the preferred alternative for the preliminary tests. An economic analysis revealed that calcium polysulfide could be produced at a fraction of the purchase cost depending on the quantities the reagents are purchased (Table 23). However, for operations with small quantities of cyanide spent liquors, the production of calcium polysulfide appears less attractive because of the cost of labour. It is quite clear, however, that the polysulfide alternative for disposal of cyanide spent liquors is much more

Table 23: Economic Analysis of Polysulfide Technology to
Treat 200 Litres of a Cyanide Spent Liquor
(CN conc'n = 50,000 mg/L)

Treatment Option	Polysulfide Content	Unit Cost !	Disposal Cost
Na-poly-S (zinc purifier)	150 g/L	\$1.05/litre	\$140.00
Ca-poly-S (limesulfur)	230 g/L	\$1.50/litre	\$130.50
Calcium Oxide Sulfur	230 g/L	\$0.13-0.30/kg \$0.39-1.04/kg	\$ 2.55- 5.86 \$26.96-73.02 ----- \$29.51-78.88*
Stablex Disposal	-	\$1.80/litre	\$360.00**

Note: * Labour and heating costs not included
 ** Freight costs for Metro Toronto area included
 ! Costs obtained from suppliers, 1986

economic than disposal at "Stablex". In addition, zinc purifier is readily available at most metal finishing shops since it is commonly used in regular operations as a plating bath purifier. From Table 23, it is evident that the zinc purifier method costs less than 40% of the "Stablex" alternative (\$140 vs \$360). Because of its availability and its economic aspects, sodium polysulfide as zinc purifier appears to be the most convenient reagent for small applications of this technology. Taking the conservative CN:poly-S⁰ ratio of 1:2 for effective application of this technology, and the current cost for zinc purifier (\$1.05/litre), this polysulfide treatment is cost effective for cyanide concentrations up to 171,000 mg/L. This very high cyanide concentration in spent liquors is uncommon in most metal finishing shops, so it can be safely stated that this simple technology is both economic and effective for most operations.

6.3 Preliminary Laboratory Results

The preliminary tests on the three types of wastewaters demonstrated that cyanide could be effectively converted to thiocyanate at CN:poly-S⁰ ratios of 1:1.5 and 1:2. For all three wastewaters, cyanide was removed after 14 days reaction time at the ratio of 1:1.5. When the polysulfide addition was increased to the CN:poly-S⁰ ratio of 1:2, both the cadmium-plating and copper-plating wastewaters had complete cyanide removal in only seven days. The zinc-plating wastewater still required two weeks for complete cyanide removal. This was attributed to the higher

initial iron concentration and/or the relatively low initial cyanide concentration. Iron-cyanide complexes are difficult to degrade, so the higher iron levels in the zinc-plating wastewater certainly have affected the reaction. This was further studied in the polysulfide-ferricyanide tests (discussed later). The low initial cyanide concentration may also have hindered the reaction, in that the driving force was reduced. This was also further examined in the dilution series of experiments.

As can be seen in the accompanying figures (Figures 1 to 6), significant metal removals were achieved in these preliminary tests. Most metals were reduced to concentrations below 10 mg/L after 28 days of reaction time. The only exception to this was iron. In all three wastewaters, iron was still persistent after the 28-day test period. This was particularly true in the zinc-plating cyanide wastewater, in which the iron remained in solution at a concentration of 571 mg/L even at the higher CN:poly-S ratio of 1:2. This fact further substantiates the above claim that iron may adversely affect the cyanide-polysulfide reaction.

By comparing the three sets of curves (Figures 1 to 6), it is seen that the higher CN:poly-S^o ratio of 1:2 is considerably more effective in reducing the metal concentrations in solution. At the lower ratio of 1:1.5, zinc remained in solution at a concentration of 188 mg/L (zinc-plating liquor), and copper

remained in solution at 36 mg/L (copper-plating liquor). With the additional polysulfide, however, zinc was further reduced to about 2 mg/L (a further 98.9% reduction), and copper down to 10 mg/L (a 72.2% reduction). In general, all metals were better removed from solution at the higher polysulfide dosage. Figures 1 to 6 also show that the reaction proceeds very quickly. In all cases, the reaction is over 90% complete after only a few days reaction time. It also appeared that the reaction was more rapid in the solutions of highest initial cyanide concentration, ie. a larger degree of removal was achieved in one day for both the cadmium and copper-plating wastewaters as compared to one day removal for the zinc-plating wastewater.

6.4 Dilution Effects

Dilution had little effect on the zinc-plating cyanide liquor treatment (see Figure 9). The initial cyanide concentration was only 7900 mg/L, however (ie. comparatively low), so this result was not totally unexpected. The copper-plating wastewater (Figure 8) did show some dilution effects. At the same CN:poly-S⁰ ratio of 1:2, more time was required to effectively convert cyanide in the diluted sample. The cadmium-plating wastewater showed the opposite (see Figure 7); faster cyanide removal was achieved in the diluted sample. When the three figures are taken together, it is apparent that at the CN:poly-S⁰ ratio of 1:2, cyanide is removed from solution faster for the cadmium and copper-plating wastewaters (7 days vs 14 days

for the zinc-plating wastewater). It is believed that the two to three times dilutions were not significant when compared to the ten-fold concentration difference between the zinc-plating wastewater and the other two. It is concluded, therefore, that cyanide is more rapidly removed (i.e. converted to thiocyanate) when the initial cyanide concentrations are higher. This statement was further substantiated by the pilot-scale results discussed later. In general, though, it was demonstrated that polysulfide treatment of spent cyanide liquors is effective on a very wide range of spent liquor concentrations; from relatively diluted (3625 mg/L CN) to highly concentrated (65,750 mg/L CN).

6.5 Temperature Considerations

As seen from the results presented thus far, initial cyanide concentrations can be very high. It was felt that a temperature problem could occur in some extreme cases. The heats of reaction for the three plating solutions were, therefore, determined (Table 13). A value of about 420 cal/g CN was calculated for both the zinc and cadmium-plating solutions. The copper-plating solution only had a heat of reaction of about 200 cal/g CN, most likely because of the energy requirements of copper/cyanide complex decomposition. Perhaps of more interest, however, are the maximum temperature rise figures. The largest temperature rise in the laboratory experiments was only 10°C (experienced in the copper-plating solution). In the second pilot-scale test (initial cyanide concentration of 181,000 mg/L) the temperature

rise was only 12° C (27° C-39° C). These temperatures do not present any problems with regard to the application of polysulfide technology. The reaction vessels used can withstand temperatures considerably higher than 40° C, and the peak temperatures decrease back to the initial temperature values soon after having been reached.

6.6 Leaching Test Results

The preliminary leaching tests (Tables 14,15 and 16) on the precipitates formed in the cyanide-polysulfide reaction showed that the metal ion concentrations in the leachate are quite low. This is primarily due to the very low solubilities of the metal sulfides. For most cases, the metal concentrations were below 1 mg/L. Iron concentrations were as high as 14 mg/L in the zinc-plating precipitate, however. Table 21 compares the leachate results to the Metropolitan Toronto Area sewer-use by-laws. It can be seen that only one value exceeds the by-law limits (ie. zinc), while all others are within the limits. With the addition of flyash, the zinc concentration dropped to 0.2 mg/L from 6.6 mg/L, which is well within the limits. The flyash helps reduce the metal ion concentrations in the leachate due to its sorption capacity and possibly also to its ion exchange capability. These preliminary results are quite encouraging, and it is believed that a rigorous solidification procedure would result in much lower leachate values.

6.7 Residual Polysulfide Considerations

In these experiments, residual polysulfide was present in the treated liquors after the completion of the reactions. As previously discussed, polysulfide could create some pollution problems if discharged directly to receiving waters. In this study, two reagents were used to remove the residual polysulfide. The first was hydrochloric acid. HCl was added to a solution of polysulfide until the pH was reduced to about 8.5. A yellow precipitate formed and the polysulfide concentration dropped from 20,054 mg/L to 160.3 mg/L (99.2% reduction). Although effective, the production of hydrogen sulfide gas made this alternative unacceptable. The second reagent used was a solution of ferrous sulfate. The results are shown in Table 17. Removals greater than 90% were accomplished by this method. Because FeSO_4 is usually available at metal finishing shops (ie. it is produced in the recovery of sulfuric acid from spent pickle liquors), the polysulfide removal is inexpensive. The procedure also results in a pH reduction which makes the effluent more acceptable for discharge.

6.8 Pilot-Scale Results

Experiments done in the laboratory at the University of Toronto showed that calcium polysulfide can be easily produced by the user. Concentrations as high as 23% polysulfide-sulfur were attained after 4-5 hours of boiling the lime suspension with elemental sulfur (Table 12). Based on these results, 20 litres

of 20% calcium polysulfide were produced for the first pilot-scale application of this technology.

The first pilot-scale test involved the application of the 20 litres of calcium polysulfide (described above) to 110 litres of a zinc-plating spent cyanide liquor. The initial cyanide concentration was 17,900 mg/L and the resulting CN:poly-S⁰ ratio was 1:2. Cyanide concentrations were reduced by 97.6% within three days reaction time. A slight decrease over the next few weeks was observed, but complete removal was not attained. It was hypothesized that this was due to the high initial iron concentrations. It was also thought that the 'homemade' polysulfide may not have been as effective as the commercially available ones. Another possibility is in the air oxygen introduction to the reacting mixture by keeping the reaction vessel open to the atmosphere.

In this pilot-scale test, as with the preliminary laboratory tests, most metals were reduced to concentrations below 10 mg/L. The exceptions here were zinc and iron. The lowest zinc concentration was determined at 16 mg/L, while the iron content remained in solution at 120 mg/L. Considering the high initial iron concentration (2600 mg/L), the iron removal achieved was good (95.4% reduction). It was postulated that a further addition of polysulfide might take the reaction to completion. This was not found to be the case, however; an additional dosage

of sodium polysulfide did not decrease the cyanide concentration. From Figure 10, it can be seen that along with decreasing cyanide concentrations, an initial thiocyanate increase occurred. The thiocyanate concentration then decreased over the duration of the experiment. The peak thiocyanate concentration also did not reach the stoichiometric amount (i.e. one thiocyanate molecule for each molecule of cyanide). It is still unclear as to the reasons behind these phenomena, but a number of explanations have been suggested. One possible explanation is that the thiocyanate is further degraded into ammonia and sulfate, but no ammonia was found in the solution. Another explanation is that some sort of polymerization occurs. A third possible explanation is that the thiocyanate either precipitates or crystallizes. This last idea is further discussed later.

The second pilot-scale application involved the addition of the zinc purifier to a cadmium-plating spent cyanide liquor (initial CN concentration of 181,000 mg/L). The CN:poly-S⁰ ratio was again set at 1:2. This second pilot-scale test was considerably more effective than the first (see Figure 11). Cyanide concentrations were reduced by 99.9% after only one day reaction time. As with the first test, however, the cyanide concentration could not be reduced to non-detectable levels. Thiocyanate also displayed similar characteristics to those in the first test (i.e. initial increase followed by a continual decrease over the duration of the experiment). The peak

thiocyanate concentrations were considerably less (7000 mg/L vs 21000 mg/L) than in the first pilot-scale test. Again this is as yet unexplained.

Metal ion removal was much more effective in the second pilot-scale test. All metals (including iron) were brought to concentrations below 5 mg/L within 10 days. The initial iron concentration was lower in this second test, however, (1400 mg/L vs 2600 mg/L). Some difficulty in treating the zinc-plating wastewater was also noted in the preliminary test, so it would appear that the combination of lower initial iron concentration and higher initial cyanide concentration does improve the effectiveness of this technology (as discussed earlier). The extent of this increased effectiveness suggests that the polysulfide used also plays a considerable role in that the less viscous form is more effective. It is thought that perhaps there is less readily available reagent for the reaction in the more viscous 'homemade' polysulfide.

A summary of the metal and cyanide removals for both pilot-scale tests is presented in Table 22. Here, a direct comparison can be made between the resulting metal cation residuals and the existing Metropolitan Toronto Area sewer-use by-laws. The first pilot-scale test fell short of our expectations in that some residuals (i.e. cyanide, iron and zinc) exceeded the by-law limits. The laboratory-produced calcium polysulfide was very viscous and contained some amount of non-reacted substrate. A

considerable amount of sludge resulted from the use of this reagent. For these reasons, the second pilot-scale test was conducted using the zinc purifier (sodium polysulfide). The results (Table 22) show that better removals can be achieved with this commercial sodium polysulfide. All metal residual concentrations were well within the by-law limits, but the total cyanide concentration in solution still exceeded the 2.0 mg/L limit. It must be noted, that under practical conditions, the treated waste would not be directly discharged to sewers. It would instead be fed slowly into the general wastewater stream which then undergoes conventional treatment. This treatment would also only be occasionally required since these spent liquors are only generated in small amounts. The actual metal residual concentrations entering the sewers would, therefore, be many times lower than those presented here.

The use of zinc purifier in the second pilot-scale application also resulted in the generation of only very little sludge. The settling tests done in graduated cylinders showed that there was volumetrically about 8% sludge produced. Because the zinc purifier is also readily available at metal finishing shops, it is considered to be the preferred alternative.

6.9 Iron Interference

To examine the possibility of iron interference in the cyanide-polysulfide reaction, the potassium ferricyanide tests were carried out (Table 20). In all cases, cyanide

concentrations were reduced but no thiocyanate was formed in the reaction. This further confirms the results of Luthy and Bruce (1978). It seems that some further metal-cyanide complexation occurs with the addition of polysulfide.

6.10 Crystallization

Another interesting, but as yet to be explained, observation was the formation of crystals on the bottom of the reaction vessel during the second pilot-scale application. Elemental analysis revealed that the primary constituents were sulfur and sodium, but there was also some iron and cyanide/thiocyanate. There were trace amounts of other metals but they were insignificant. It is not known if the cyanide/thiocyanate and metals are merely impurities, or if they are part of the crystal structure. The crystals themselves are yellow and quite soluble in water. Because of the presence of cyanide (or thiocyanate), these crystals may hold the key to the decreasing thiocyanate concentrations observed in this study. X-ray diffraction techniques have not yet provided us with an indication as to the structure of these crystals, but future tests should shed light on this subject.

7.0 SUMMARY AND CONCLUSIONS

This study was conducted to examine the effectiveness of the cyanide-polysulfide reaction in the treatment of concentrated spent cyanide liquors, generated from metal finishing shops, that contain metal compounds, presumably in the form of metal-cyanide complexes. The primary objective of this technology was to treat the cyanide liquor and produce an effluent quality acceptable for discharge to municipal sanitary sewer systems. The following conclusions were made from the experiments performed:

1. There are effectively no differences in treatment efficiency between the use of calcium polysulfide or sodium polysulfide as reagents for this technology. Although calcium polysulfide can be produced on-site at a fraction of the purchase cost, sodium polysulfide as "zinc purifier" is the preferred alternative since higher metal and cyanide removals can be achieved and because the use of this reagent is associated with the generation of very little sludge (~8%).
2. The higher cyanide to polysulfide ratios ($\text{CN}:\text{poly-S}^0=1:2$) were more effective in cyanide conversion; reaction times were shorter and metal reductions were improved.
3. Polysulfide treatment is effective on a wide range of cyanide-containing wastewaters; good results were obtained on wastewaters containing cyanide ranging from 3625 mg/L to 181,000

mg/L. The reaction is more rapid, however, at high initial cyanide concentrations.

4. Pilot-scale tests confirmed that over 99.9% cyanide removal can be achieved, as well as reductions to less than 2 mg/L for each metal cation, in under two weeks reaction time.

5. Over 95% removal of residual polysulfide from treated liquors can be accomplished by the addition of ferrous sulfate.

6. Metal ion concentrations in the leachate from the precipitates formed in the cyanide-polysulfide reaction are low. Most metal concentrations were below 3 mg/L, and all were within the limits set by the Metropolitan Toronto sewer-use by-laws. The addition of flyash reduces metal ion concentrations in some instances.

7. The cyanide-polysulfide reaction is mildly exothermic, but no operating problems are foreseen since only slight temperature increases are expected. A temperature increase of only 12° C was noted in the second pilot-scale test.

The cyanide-polysulfide reaction provides a safe, effective, and practical means of detoxifying highly concentrated waste cyanide solutions. The simplicity of the process and the ready

availability of the polysulfide reagent make this technology appropriate for use in some small electroplating shops or in developing countries.

8.0 RECOMMENDATIONS

Further studies should be conducted to:

1. monitor this process in a full-scale application such as at X-Pert Metals (Burlington, Ontario).
2. study the sludge generated by the use of this technology in greater depth. A full-scale operation is expected to produce sufficient sludge for extensive study.
3. investigate further the possibility of solidifying the generated sludge so that it can be disposed of in an appropriate manner.
4. examine the formation of crystals in the supernatant of the reaction products. Preliminary work on these crystals have not led to their identification; both chemistry and x-ray diffraction techniques have thus far been unsuccessful. A number of other tests are available, and it is hoped that perhaps this work will also give further insight as to the fate of thiocyanate formed.
5. pursue the possibility of polymerization and/or precipitation to explain the apparent loss of thiocyanate.
6. examine the polysulfide/metal-cyanide complex reaction in more detail.
7. explain the residual cyanide concentrations in the pilot-scale tests.

8. examine any possible reactions between the products of polysulfide application (thiocyanate and excess polysulfide) and contaminants downstream, with special interest in the possible consequences of accidental acidification, temperature extremes or contact with other active compounds.

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